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ENTHALPIES OF COMBUSTION OF EXO-THDC, RJ-4, ISOMERIZED RJ-4, AN--ETC(U)
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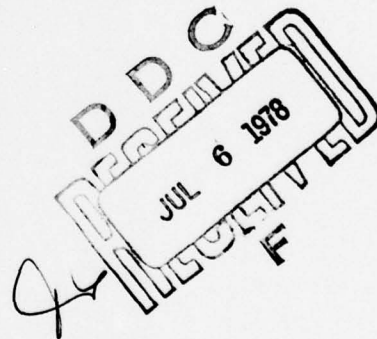
ENTHALPIES OF COMBUSTION OF *exo*-THDC, RJ-4,
ISOMERIZED RJ-4, AND JP-9

by

N. K. Smith and W. D. Good

- (3) Bartlesville Energy Research Center.
① Department of Energy
② Bartlesville, Oklahoma

410 743



Research sponsored by:

Air Force Office of Scientific Research (NA)
Department of the Air Force
Contract No. AFOSR-ISSA-78-0009

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June 1978

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

<p>18 REPORT DOCUMENTATION PAGE</p>		<p>READ INSTRUCTIONS BEFORE COMPLETING FORM</p>	
<p>1 AFOSR-TR-78-1069</p>		<p>2. GOVT ACCESSION NO.</p>	
<p>4. TITLE (and Subtitle)</p> <p>6 ENTHALPIES OF COMBUSTION OF exo-THDC, RJ-4, ISOMERIZED RJ-4, AND JP-9.</p>		<p>5. TYPE OF REPORT & PERIOD COVERED</p> <p>9 INTERIM Repts</p>	
<p>7. AUTHOR(s)</p> <p>10 N. K. SMITH W. D. GOOD</p>		<p>6. PERFORMING ORG. REPORT NUMBER</p>	
<p>9. PERFORMING ORGANIZATION NAME AND ADDRESS</p> <p>DEPARTMENT OF ENERGY BARTLESVILLE ENERGY RESEARCH CENTER P. O. BOX 1398, BARTLESVILLE, OK 74003</p>		<p>15 AFOSR-ISSA-78-0009 <i>new</i></p>	
<p>11. CONTROLLING OFFICE NAME AND ADDRESS</p> <p>AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D C 20332</p>		<p>PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS</p> <p>16 2308B1 17 B1 61102F</p>	
<p>14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)</p> <p>12 17p.</p>		<p>12. REPORT DATE</p> <p>17 JUNE 78</p>	
<p>16. DISTRIBUTION STATEMENT (of this Report)</p> <p>Approved for public release; distribution unlimited.</p>		<p>13. NUMBER OF PAGES</p> <p>18 18</p>	
<p>18. SUPPLEMENTARY NOTES</p>		<p>15. SECURITY CLASS. (of this report)</p> <p>UNCLASSIFIED</p>	
<p>19. KEY WORDS (Continue on reverse side if necessary and identify by block number)</p> <p>exo-THDC RJ-4 RJ-4-I JP-9</p>		<p>RAMJET FUELS GROSS HEAT OF COMBUSTION NET HEAT OF COMBUSTION</p>	
<p>20. ABSTRACT (Continue on reverse side if necessary and identify by block number)</p> <p>The enthalpies of combustion of four liquid ramjet fuels, exo-THDC, RJ-4, RJ-4-I, and JP-9, were measured by precision oxygen-bomb combustion calorimetry. The following values are reported for the net enthalpy of combustion at 298.15 K (25° C): exo-THDC, $-(10081.5 \pm 2.3)$ cal g⁻¹; RJ-4, $-(10153.1 \pm 2.3)$ cal g⁻¹, RJ-4-I, $-(10141.4 \pm 2.2)$ cal g⁻¹; and JP-9, $-(10089.3 \pm 2.4)$ cal g⁻¹.</p> <p>410 743</p>			

SCIENTIFIC REPORT

ENTHALPIES OF COMBUSTION OF *exo*-THDC, RJ-4,
ISOMERIZED RJ-4, AND JP-9

Bartlesville Energy Research Center
Department of Energy
Bartlesville, Oklahoma

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ISOMERIZED RJ-4, AND JP-9^a

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The enthalpies of combustion of four liquid ramjet fuels, *exo*-THDC, RJ-4, RJ-4-I, and JP-9, were measured by precision oxygen-bomb combustion calorimetry. The following values are reported for the net enthalpy of combustion at 298.15 K (25° C): *exo*-THDC, $-(10081.5 \pm 2.3) \text{ cal g}^{-1}$; RJ-4, $-(10153.1 \pm 2.3) \text{ cal g}^{-1}$; RJ-4-I, $-(10141.4 \pm 2.2) \text{ cal g}^{-1}$; and JP-9, $-(10089.3 \pm 2.4) \text{ cal g}^{-1}$.

1. INTRODUCTION

In cooperation with the Air Force Office of Scientific Research, this laboratory has studied compounds with high enthalpies of combustion per unit mass^(1,2) and per unit volume.^(3,4) This report gives the details of experimental measurements of the enthalpies of combustion of four hydrocarbon liquids being evaluated as ramjet fuels.

^a Work conducted under an Interagency Agreement, AFOSR-ISSA-78-0009, between the Air Force Office of Scientific Research (AFSC) and the Department of Energy.

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2. EXPERIMENTAL

MATERIALS

All four fuels studied are liquids. Carbon skeletons of three are shown in Figure 1. *exo*-THDC, *exo*-tetrahydrodicyclopentadiene, is a pure compound. RJ-4, *exo*-tetrahydrodi(methylcyclopentadiene), and RJ-4-I, *endo*-tetrahydrodi(methylcyclopentadiene) are mixtures of isomers in which the location of the methyl groups is unknown. JP-9 is a blend of 10.3 weight percent methylcyclohexane, 68.4 weight percent of *exo*-THDC, and 21.2 weight percent of the hydrogenated dimers of norbornadiene whose empirical formula is $C_{14}H_{18}$. Carbon skeletons of typical isomers are shown in Figure 2. The empirical formula for the blend is $C_{10.529}H_{16.202}$.

exo-THDC, RJ-4, and RJ-4-I were provided by G. W. Burdette, Propulsion Development Department, Naval Weapons Center, China Lake, California. The JP-9 sample was obtained from James R. McCoy, Fuels Branch, Fuels and Lubrication Division, Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio; it is from Sun Oil Co. Batch 24. All materials were used as received.

Carbon dioxide was recovered from the combustion products of typical calorimetric experiments with all four fuels. Quantitative carbon dioxide recovery is a good indication that combustion was complete, that the sample was dry, and that sample composition was understood. A summary of carbon dioxide recovery is given in Table 1. The value for JP-9 is noticeably lower than the recoveries from the other three fuels.

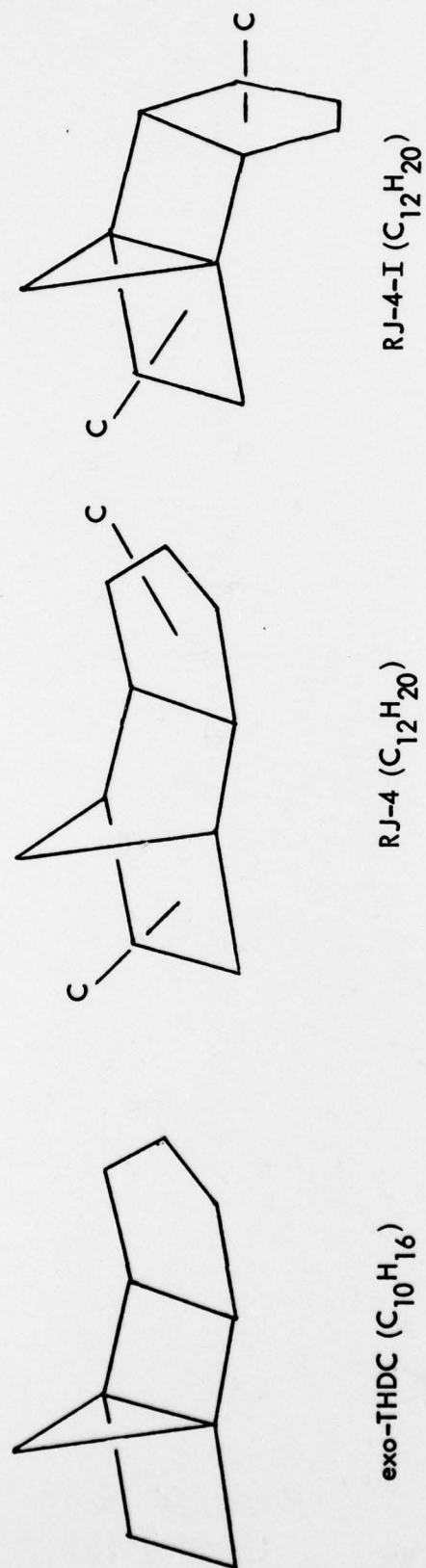


FIGURE 1. Carbon skeletons of hydrocarbon fuels.

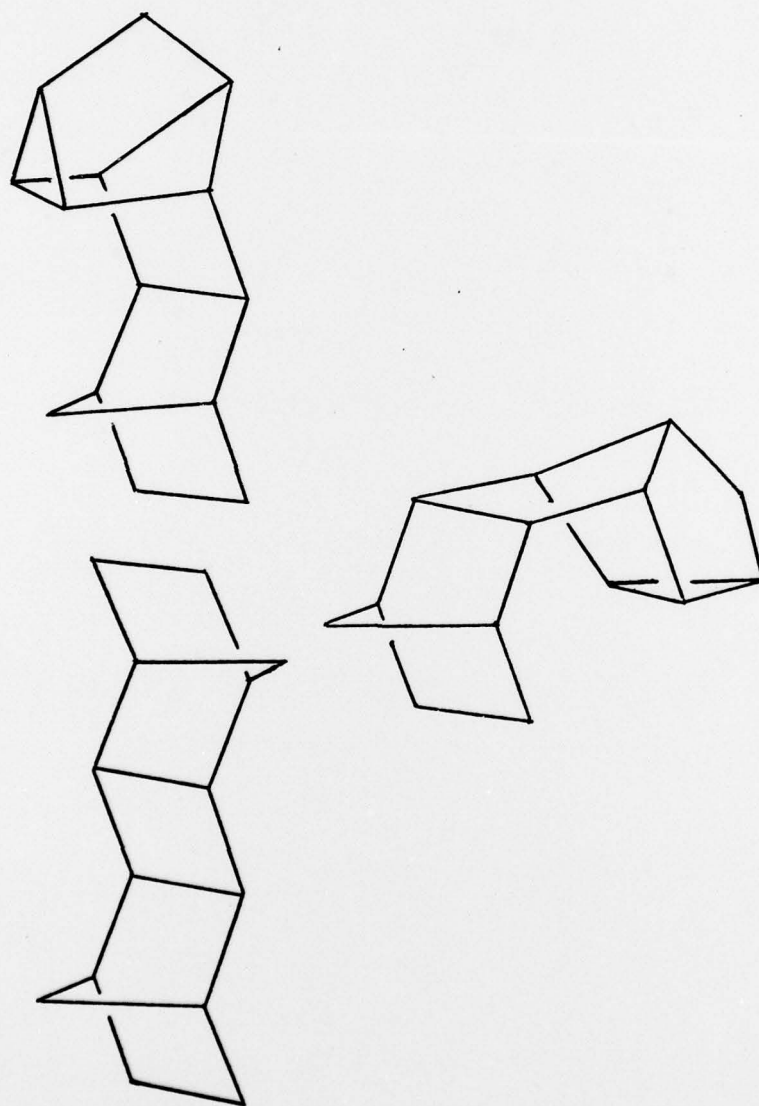


FIGURE 2. Carbon skeletons of typical isomers of hydrogenated dimer of norbornadiene.

TABLE 1. Carbon dioxide recovery

Fuel	Number of experiments	Percent recovery ^a
exo-THDC	6	99.99 ₁
RJ-4	6	99.98 ₃
RJ-4-I	3	99.96 ₂
JP-9	4	99.63 ₀

^a Mean value.

National Bureau of Standards benzoic acid sample 39i was used for calibration. Its certified energy of combustion, $-(26434 \pm 3) \text{ J g}^{-1}$, was converted to standard conditions⁽⁵⁾ giving $-(6313.02 \pm 0.72) \text{ cal g}^{-1}$ for $\Delta E_c^\circ/\text{M}$, the specific energy of the idealized combustion reaction.

Previous combustion experiments on the auxiliary oil, laboratory designation TKL 66, gave a value for $\Delta E_c^\circ/\text{M}$ of $-(11004.41 \pm 0.42) \text{ cal g}^{-1}$.

For the cotton thread fuse, empirical formula $\text{CH}_{1.774}\text{O}_{0.887}$, $\Delta E_c^\circ/\text{M} = -4050 \text{ cal g}^{-1}$.

APPARATUS AND PROCEDURE

Experimental procedures used for the combustion calorimetry of hydrocarbons by this laboratory have been described.^(6, 7) Rotating-bomb calorimeter BMR II⁽⁸⁾ and platinum-lined bomb Pt-3b,⁽⁹⁾ internal volume 0.349_4 dm^3 , were used without bomb rotation. For each experiment, 1 cm^3 of water was added to

the bomb, and the bomb was flushed and charged to 30 atm (3040 kPa) with pure oxygen. Because the oxygen was pure, nitric acid formation was negligible. Each experiment was started at 296.15 K, and the final temperatures were very nearly 298.15 K. Fragile flexible ampoules^(6, 10) of borosilicate glass confined the liquid samples. In filling ampoules with JP-9, the apparatus was charged with enough methylcyclohexane to provide its saturation vapor pressure before introducing the sample in order to minimize the evaporation of that component from the fuel.

UNITS OF MEASUREMENT AND AUXILIARY QUANTITIES

The results are based on the 1961 atomic weights⁽¹¹⁾ and the 1963 definition of the thermochemical calorie ($\text{cal} = 4.184 \text{ J}$).⁽¹²⁾ The reference temperature is 298.15 K (25° C). For reducing weights in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states,⁽⁵⁾ the values in Table 2 were used for density ρ , specific heat capacity c_p , and $(\partial E/\partial P)_T$. The values of density were obtained from the mass of material contained by ampoules of known volume. Values of c_p for exo-THDC and RJ-4 were from differential scanning calorimetry. Values of c_p for RJ-4-I and JP-9 are estimates as are all values of $(\partial E/\partial P)_T$.

CALIBRATION

One set of calibration experiments with benzoic acid was run concurrently with the series of experiments with exo-THDC and RJ-4. The calibration result was $E(\text{calor}) = 4008.11 \pm 0.20) \text{ cal}_{\text{th}} \text{ K}^{-1}$ (mean and standard deviation of the mean). A second set of calibration experiments was run concurrently with

TABLE 2. Physical properties at 298.15 K^a
 (cal_{th} = 4.184 J; atm = 101.325 kPa)

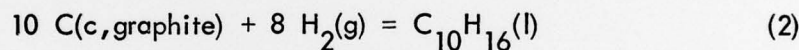
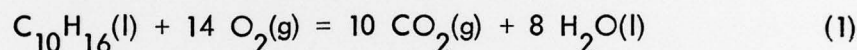
Fuel	ρ g cm ⁻³	$(\partial E/\partial P)_T$ cal _{th} atm ⁻¹ g ⁻¹	c_p cal _{th} K ⁻¹ g ⁻¹
exo-THDC	0.939	(-0.003)	(0.42)
RJ-4	0.920	(-0.003)	(0.44)
RJ-4-I	0.917	(-0.003)	(0.30)
JP-9	0.946	(-0.003)	(0.30)

^a Values in parentheses are estimates.

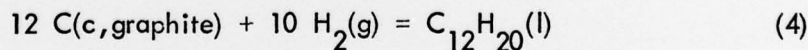
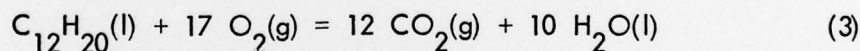
the series of experiments with RJ-4-I and JP-9. The calibration result was $\mathcal{E}(\text{calor}) = (4007.02 \pm 0.26) \text{ cal}_{\text{th}} \text{ K}^{-1}$ (mean and standard deviation of the mean).

3. CALORIMETRIC RESULTS

Results of typical experiments with the four fuels are summarized in Table 3. Values of $\Delta E_c^\circ/\text{M}$, the specific energy of the idealized combustion reaction, for all experiments are given in Table 4; all values refer to the reaction of unit mass of sample. The idealized combustion and formation reactions for exo-THDC are represented by equations 1 and 2, respectively. The idealized



combustion and formation reactions for RJ-4 and RJ-4-I are represented by equations 3 and 4, respectively.



The reader should be reminded that RJ-4 and RJ-4-I are mixtures of isomers. The idealized combustion reaction for JP-9 is represented by equation 5.

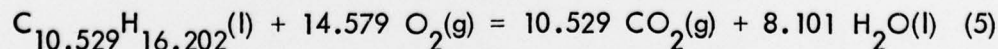


TABLE 3. Summary of typical calorimetric experiments at 298.15 K^a(cal_{th} = 4.184 J)

	exo-THDC	RJ-4	RJ-4-I	JP-9
m' (fuel)/g	0.693077	0.671733	0.661629	0.675054
m'' (auxiliary substance)/g	0.056663	0.071059	0.081998	0.073573
m''' (fuse)/g	0.001316	0.001200	0.001250	0.001078
n ⁱ (H ₂ O)/mol	0.05535	0.05535	0.05535	0.05535
$\Delta T_c / K = (T_f - T_i + \Delta T_{corr}) / K$	2.00216	2.00052	2.00235	1.99890
$\mathcal{E}(\text{calor})(-\Delta T_c) / \text{cal}_{th}$	-8024.89	-8018.33	-8023.45	-8009.63
$\mathcal{E}(\text{cont})(-\Delta T_c) / \text{cal}_{th}$ ^b	-10.20	-10.19	-10.00	-10.02
$\Delta E_{ign} / \text{cal}_{th}$	0.18	0.18	0.18	0.18
$\Delta E_{(corr \text{ to std states})} / \text{cal}_{th}$ ^c	3.02	2.90	2.91	3.09
$\{-m''(\Delta E_c^\circ / M)(\text{auxiliary substance})\} / \text{cal}_{th}$	623.54	781.96	902.33	809.63
$\{-m'''(\Delta E_c^\circ / M)(\text{fuse})\} / \text{cal}_{th}$	5.33	4.86	5.06	4.36
$\{m'(\Delta E_c^\circ / M)(\text{fuel})\} / \text{cal}_{th}$	-7403.02	-7238.62	-7122.97	-7202.39
$\{(\Delta E_c^\circ / M)(\text{fuel})\} / \text{cal}_{th} \text{ g}^{-1}$	-10681.37	-10776.04	-10765.81	-10669.36

^a The symbols and abbreviations of this table are those of reference 3 except as noted. ^b $\mathcal{E}(\text{cont})(T_i - 298.15 \text{ K}) - \mathcal{E}(\text{calor})(298.15 \text{ K} - T_i + \Delta T_{corr})$. ^c Items 81 to 85, 87 to 90, 93, and 94 of the comparison form of reference 3.

TABLE 4. Summary of experimental results at 298.15 K
 $(\text{cal}_{\text{th}} = 4.184 \text{ J})$

	$(\Delta E_c^\circ/M)/\text{cal}_{\text{th}} \text{ g}^{-1}$			
	exo-THDC	RJ-4	RJ-4-I	JP-9
	-10685.70	-10776.90	-10764.58	-10672.20
	81.04	74.78	63.98	68.51
	79.84	76.04	65.81	69.36
	83.59	76.14	62.83	66.61
	81.37	77.91	62.17	70.21
	-10680.53	-10772.28	-10762.49	-10668.09
Mean	-10682.01	-10775.68	-10763.64	-10669.16
Standard deviation of the mean	0.90	0.80	0.57	0.78

4. DERIVED RESULTS

Derived values of the standard molar energy of the idealized combustion reaction, ΔE_c° , the standard molar enthalpy of combustion, ΔH_c° , and the standard molar enthalpy of formation, ΔH_f° , (exo-THDC, RJ-4, and RJ-4-I only), of the fuels in the liquid state are given in Table 5. Values of ΔE_c° and ΔH_c° refer to equations 1, 3, and 5; the values of ΔH_f° refer to equations 2 and 4. The uncertainties given in Table 5 are the "uncertainty intervals."⁽¹³⁾ The enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ were taken to be -94.051 and -68.315 $\text{kcal}_{\text{th}} \text{mol}^{-1}$, respectively.⁽¹⁴⁾ Uncertainties assigned to the respective values were 0.011 $\text{kcal}_{\text{th}} \text{mol}^{-1}$ for CO_2 ⁽¹⁵⁾ and 0.010 $\text{kcal}_{\text{th}} \text{mol}^{-1}$ for $\text{H}_2\text{O}(\text{l})$.⁽¹⁶⁾

The values of enthalpy of combustion given in Tables 3, 4, and 5 are the "gross" heats of combustion for which the reaction products are gaseous carbon dioxide and liquid water. For combustion yielding gaseous carbon dioxide and gaseous water, the values of the "net" heat of combustion are: exo-THDC, $-(10081.5 \pm 2.3) \text{ cal g}^{-1}$; RJ-4, $-(10153.1 \pm 2.3) \text{ cal g}^{-1}$; RJ-4-I, $-(10141.4 \pm 2.2) \text{ cal g}^{-1}$; and JP-9, $-(10089.3 \pm 2.4) \text{ cal g}^{-1}$.

TABLE 5. Derived molar values for the liquid state at 298.15 K
 $(\text{cal}_{\text{th}} = 4.184 \text{ J})$

Fuel	ΔE_c°	ΔH_c°	ΔH_f°
	$\text{kcal}_{\text{th}} \text{ mol}^{-1}$	$\text{kcal}_{\text{th}} \text{ mol}^{-1}$	$\text{kcal}_{\text{th}} \text{ mol}^{-1}$
exo-THDC	-1455.31 ± 0.33	-1457.68 ± 0.33	-29.35 ± 0.35
RJ-4	-1770.37 ± 0.37	-1773.33 ± 0.37	-38.43 ± 0.40
RJ-4-I	-1768.39 ± 0.36	-1771.36 ± 0.36	-40.41 ± 0.39
JP-9	-1523.52 ± 0.34	-1525.92 ± 0.34	-----

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